

A novel TG–GC/MS system

Quantification of low-content styrene–butadiene rubber in natural rubber

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Abstract Thermogravimetric analysis (TG) is a common technique to characterize the composition of polymers. To obtain more information about the decomposition products (and by this to get more information of the original composition of the original polymer), the TG is frequently coupled to a mass spectrometer (MS) and/or an infrared spectrometer (FTIR). However, TG–MS and TG–FTIR do not permit to identify the decomposition products separately. Especially with decomposition products present in low concentration, their identification by FTIR or MS is virtually impossible. This problem can be avoided by combing gas chromatography (GC) and MS. In this configuration, GC is used to separate different decomposition products that are then unambiguously identified by the MS. In the past, GC/MS coupled to TG offered only few GC injections or poor separation. A novel system includes a heated storage interface. This interface can store up to 16 gas aliquots collected at distinct temperatures during the course of a TG experiment. In this contribution, we present this new approach to combine a TG with a GC/MS. The potential of this novel combination is illustrated on the example of natural rubber samples with less than 10 % SBR content styrene–butadiene rubber (SBR). Using one SBR-specific decomposition product (styrene), quantification of the SBR content is possible. Also, emission profiles of in principle any decomposition product can be obtained and compared with the TG and the DTG curve.

Keywords TG–GC/MS · Compositional analysis · Blend quantification

Introduction

Small variations in polymer and filler content can extend the performance of elastomers. Quantitative analysis of blend composition is therefore of a vital matter to the elastomer industry. Varieties of analytical tools have been developed to monitor rubber blend composition. Fourier transformation infrared (FTIR) spectroscopy, thermogravimetric analysis (TG), pyrolysis gas chromatography–mass spectrometry (Py-GC/MS), differential scanning calorimetry (DSC) and attenuated total reflectance (ATR) are often used to monitor blend composition [1–21]. These techniques have proven their efficiency; however, many of studies have been analyzed using blend of ratios superior to 10 % [22–30].

Thermogravimetric analysis (TG) is often used to characterize the composition of blends. In TG, the mass change of a sample is measured while it is heated at constant heating rate or maintained isothermally in either an inert (nitrogen, argon) or an oxidative (air, oxygen) atmosphere.

For a better understanding of the nature of decomposition gases evolved from the TG measurement, Fourier transformation infrared spectroscopy (FTIR) and mass spectrometry (MS) are two common methods often used [31–34]. Simultaneous information about degradation products is obtained during the sample mass change. TG–FTIR and TG–MS are used for identification, qualitative and quantitative analysis of evolved gases as well as for the comprehension and elucidation of the decomposition process. TG–FTIR and TG–MS are very effective techniques only if few, known volatile compounds are evolved or to

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understand some decomposition routes [35]. These techniques allow the emission profile of compounds among the thermal gravimetric decomposition to be drawn. However, especially with polymers, many decomposition products evolve simultaneously. Consequently, in the best case only the main products can be identified and these can overlap compounds with low concentration which cannot be detected.

A chromatographic separation is therefore necessary to identify the simultaneously evolved products. A well-established method is pyrolysis gas chromatography mass spectrometry (Py-GC/MS) [36]. This technique consists of heating the sample very quickly from room temperature to high temperature in a tube or directly on a filament. The decomposition products can then be trapped by cooling at the beginning of the GC column or directly introduced into the GC capillary column. In most pyrolysis systems, only helium or air can be used as carrier gas. Py-GC/MS allows the detection, identification and even quantification of all thermal decomposition products and is a very sensitive analysis [37–39]. Nevertheless, Py-GC/MS does not allow the monitoring emission of decomposition products as a function of temperature without considerable time and efforts. High and time-consuming maintenance due to blocked capillaries or polluted injection systems by high boiling products is the main disadvantage of this technique [40].

Efforts have been made to couple a TG to a GC or GC/MS system [41–44]. Currently, commercial TG–GC/MS coupling systems are limited regarding the number of GC/MS measurements that can be done during thermogravimetric analysis.

Here a novel approach in which the TG is coupled to the GC/MS by means of a heated storage interface (IST) generally at 250 °C is presented.

The decomposition products from the TG decomposition are transferred to the IST storage oven via a heated transfer line. When the IST is in this “storage” mode, the gases coming from the TG are released through the outlet of the interface. At a predefined time, which corresponds to a defined temperature in the TG, fractions of the volatile decomposition products are stored in a heated loop. Up to 16 loops containing 250 μL of gases can be used. These storage times are selected by the user and are determined during a first TG experiment using the same method.

Once the last loop has been collected, the interface switches to the “inject” mode. The decomposition gases stored in the first loop are injected into the GC via a second heated transfer line by the GC carrier gas. The individual gases are first separated by the GC and then analyzed by the MS detector. Spectral libraries are generally used for their identification. At the end of the first GC/MS measurement, the second loop is then injected into the GC and

so on. With this setup, volatile products with masses up to $m/z = 250$ can be detected.

The emission profile of selected evolved compounds can be followed using the 16 loops as a function of the thermogravimetric decomposition temperature. The storage interface, unlike other evolved analysis method, may be used with any gas allowed in the TG. Decomposition in different matrices may lead to different evolved compounds and therefore different evolved profiles [45].

This study illustrates the feasibility of using TG–IST–GC/MS to estimate the amount of styrene–butadiene (SBR) in natural rubber (NR)/SBR copolymer blends containing very low amounts of SBR.

Experimental

Materials

The rubber samples were supplied by the Malaysian Rubber Board (MRB), 18th Floor Bangunan Getah Asli (Menara), 148 Jalan Ampang, 50450 Kuala Lumpur, Malaysia.

The rubbers were manufactured in the MRB research and development pilot production center. The samples consisted of unfilled natural rubber (NR) and styrene–butadiene (SBR) single elastomer and three different copolymer blends of NR containing low amounts of SBR. The SBR contents were 2.5, 5.5 and 7.5 %, respectively. NR content was 97, 94 and 92 %, respectively. The other constituents consisted of stearic acid (0.5 %), sulfur, accelerator and low volatiles such as oils.

Experimental method

TG

The TG/DSC 3+ from Mettler Toledo was used. In a first experiment, a 20 mg sample was heated in the TG from 25 to 600 °C at 10 K min^{-1} in a 70- μL alumina crucible. Nitrogen was used as balance purge and sample purge gas at 10 and 30 mL min^{-1} flow rate, respectively. This first experiment allows the determination of the storage times (corresponding to a certain TG temperature) for the TG–GC/MS analysis to follow.

TG–GC/MS

In a second experiment, the TG was coupled to an Agilent gas chromatography 7890 GC and an Agilent mass selective detector 5975C MSD using the IST16 interface from SRA Instruments (Fig. 1). The amount of sample and

Fig. 1 TG–IST–GC/MS system

the TG method used in this second experiment were the same as for the first.

The IST transfer line and oven temperatures were set at 250 °C. The GC split/splitless injector temperature was set to 280 °C. The GC oven temperature program consisted of an isothermal step at 50 °C for 5 min followed by a heating to 300 °C at 10 °C/min and another isothermal at 300 °C for 5 min. The column was an HP-5 ms of 60 m × 0.32 mm × 0.25 μm. Helium was used as carrier gas in the pressure control mode to ensure a column flow of 1.0 mL min⁻¹. At the GC injector, helium was split 5:1. The MS was operated in scan mode from 33 *m/z* to 350 *m/z*. Ionization was effectuated by electron impact (EI) at 70 eV, and an electron multiplier voltage (EMV) of 1 was used. The temperature of the ion source was set at 230 °C and the quadrupole at 150 °C.

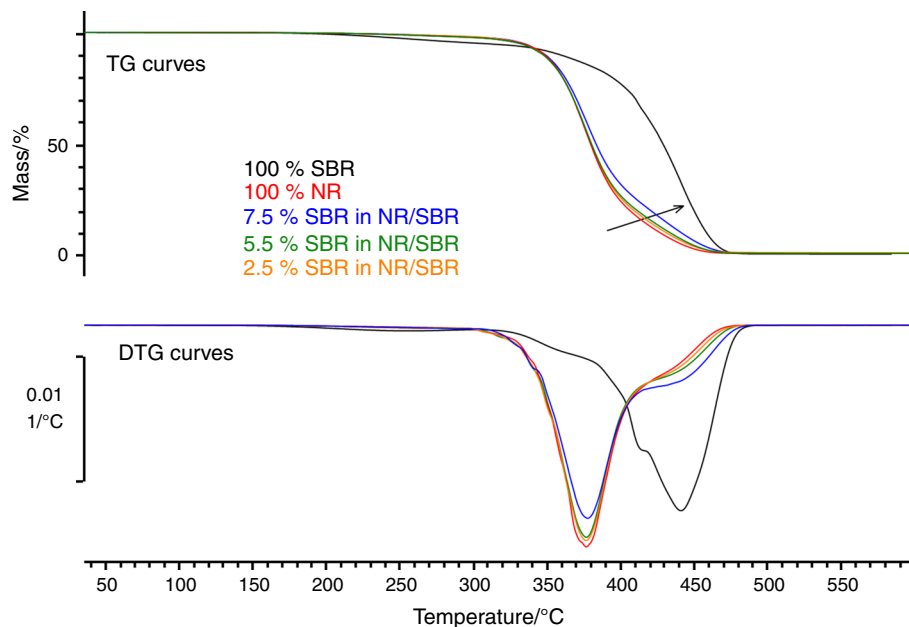
The compounds in the GC/MS total ion chromatogram (TIC) were identified using NIST/EPA/NIH Mass Spectral Library 2011 [46].

Results and discussions

TG

The TG and the corresponding DTG curves are presented in Fig. 2. For NR and NR/SBR blend, the first decomposition step up to about 350 °C is caused by the elimination of moisture and volatiles (2 %). Then, the pyrolysis of the elastomer takes place with a typical decomposition profile for NR (97 %). For SBR, the volatilization step is about 5 % and the decomposition of the polymer is about 94 %.

NR and SBR as single elastomers clearly show two different decomposition profiles. NR and NR/SBR show similar decomposition profiles. Only a shift in the TG curve with increased concentration of SBR in the blend at the end of the decomposition is observed (indicated by the arrow in Fig. 2).

Fig. 2 TG curves of NR and SBR single elastomers and NR/SBR blend at different ratios

TG-IST-GC/MS

Identification of evolved compounds in NR and SBR

Based on TG decomposition profiles shown in Fig. 3, storages of the decomposition products for all samples were set according to the TG temperatures as shown in Table 1.

After collection of the last loop (number 16), each loop was injected individually. The evolved gas compounds were separated by the GC column and then identified by the MS using the NIST/EPA/NIH Mass Spectral Library 2011.

Figure 3 displays the total ion chromatogram (TIC) of loop 10 of the 100 % NR sample in (a) which corresponds to a TG temperature of 370 °C and in (b) the TIC of loop 12 of the 100 % SBR sample which corresponds to a TG temperature of 400 °C. The main five compounds identified using the NIST/EPA/NIH Mass Spectral Library 2011 are summarized in Table 1 together with the retention times (RT) in minutes, the chemical formula, the structure and

Fig. 3 **a** TIC of loop 10 (370 °C) of 100 % NR; **b** TIC of loop 12 (400 °C) of 100 % SBR

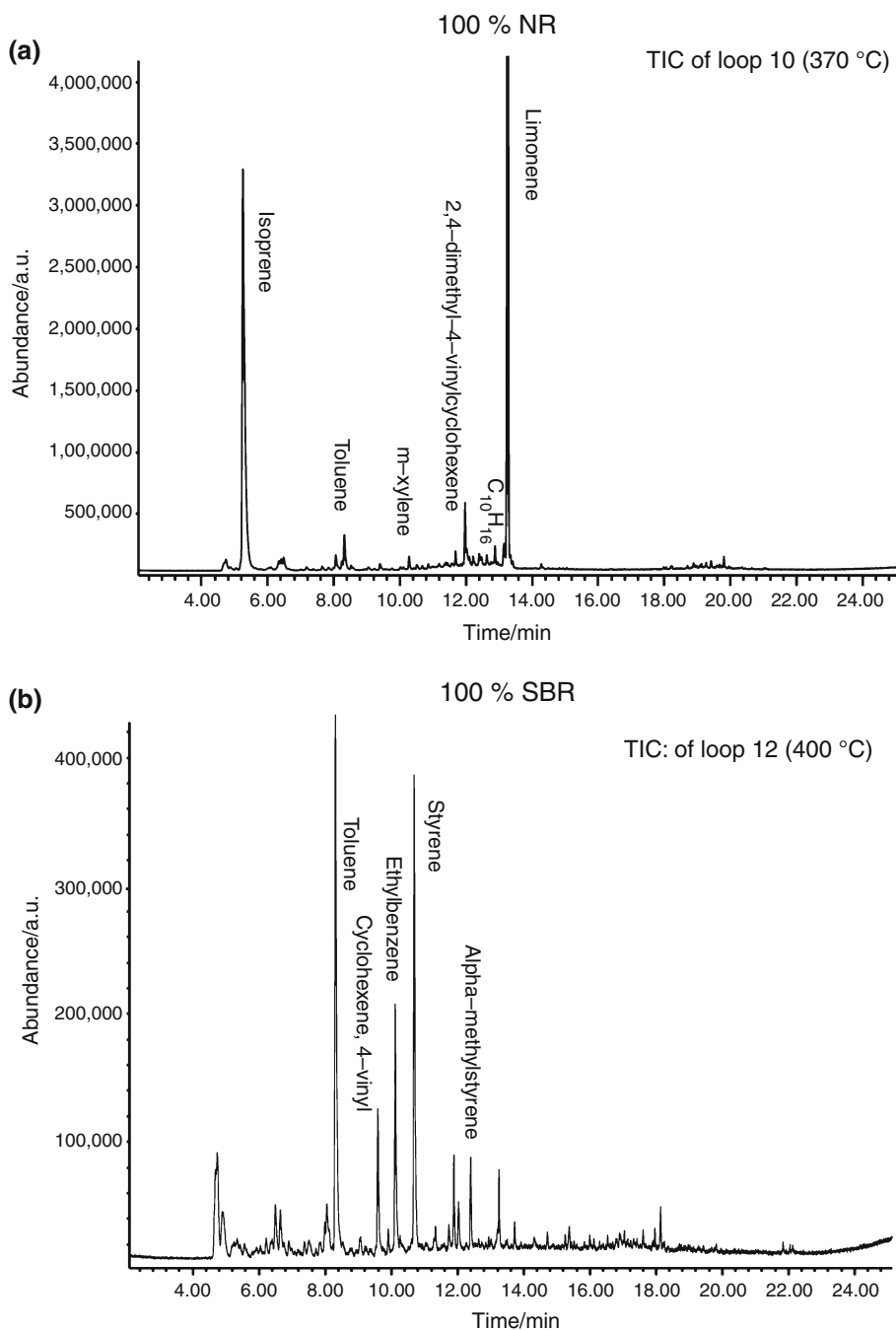


Table 1 Storage of evolved products according to the TG temperatures

IST16 loop number	TG temp. in °C
2	260
3	280
4	300
5	320
6	330
7	340
8	350
9	360
10	370
11	380
12	400
13	420
14	440
15	460
16	500

the main m/z . All of these five compounds had a quality factor above 90 % (Table 2).

In the 100 % NR, limonene (dimers) is the main evolved decomposition product. Other main evolved compounds are isoprene and m-xylene. Evaluation of the GC/MS analysis results of the 100 % SBR showed that these compounds are not evolved during its decomposition. The main component evolved is toluene. Toluene is not specific to SBR as it is also evolved during NR decomposition. The

main evolved decomposition product specific to SBR is styrene.

Identification of evolved compounds in NR/SBR blend

In Fig. 4, the TIC of loop 12 of the NR/SBR containing 2.5 % SBR is shown. The main evolved compounds of NR such as limonene are clearly detected. Styrene which comes from SBR is also clearly identified (Fig. 5). The upper part of Fig. 5 displays the mass spectrum of the corresponding 10.7-min retention time peak of the TIC. The base peak is m/z 104, and the main fragment peaks are m/z 103, m/z 78, m/z 77 and m/z 51. This mass spectrum is identified using the spectral library NIST/EPA/NIH Mass Spectral Library 2011. The best fit shown in the lower part of Fig. 5 is styrene (unique identifier #4830) with a match quality of 94.

Emission profile

Using the 15 storage loops, decomposition profiles of selected products are determined as a function of temperature.

The response factor $Rf_{i,l}$ of compound i in each individual loop l is calculated by the area of the main m/z peak A normalized by the initial sample mass, m_s :

$$Rf_{i,l} = \frac{A}{m_s} \quad (1)$$

The ratios $k_{i,l}$ are calculated by dividing the individual response factors $Rf_{i,l}$ by the sum of the response factors $\sum Rf_{i,l}$:

Table 2 Selection of some evolved compounds


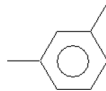
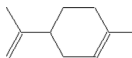

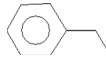
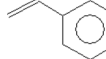
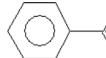
Compound name	RT/min	Main m/z	Formula	Structure
<i>100 % NR</i>				
Toluene	8.32	91	C_7H_8	
m-xylene	10.28	91	C_8H_{10}	
2,4-dimethyl-4-vinylcyclohexene	11.98	68	$C_{10}H_{16}$	
$C_{10}H_{16}$ (dimer)	12.90			
Limonene	13.28			
<i>100 % SBR</i>				
Toluene	8.32	91	C_7H_8	
Ethylbenzene	10.13	91	C_8H_{10}	
Styrene	10.70	104	C_8H_8	
Alpha-methylstyrene	12.40	118	C_9H_{10}	

Fig. 4 TIC of loop 12 (400 °C) of NR/2.5 % SBR blend

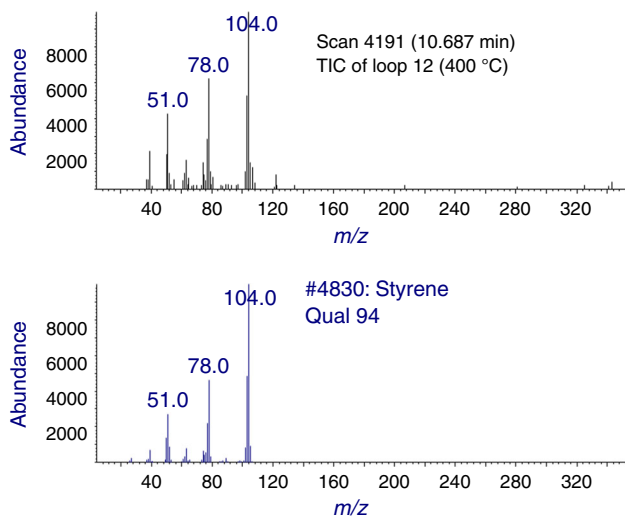
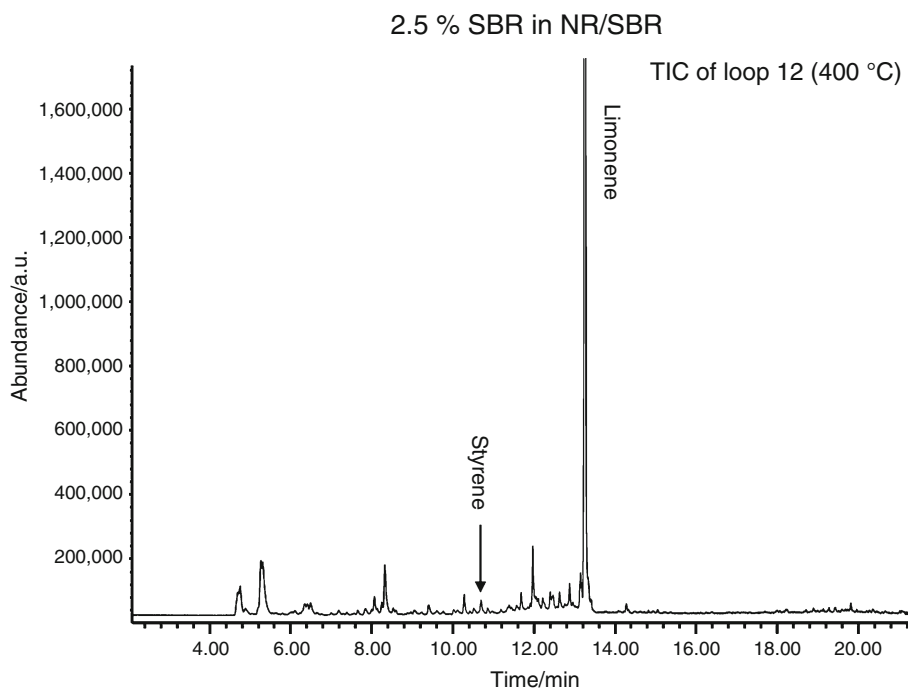


Fig. 5 Identification of styrene using the NIST/EPA/NIH Mass Spectral Library 2011

$$k_{i,l} = \frac{Rf_{i,l}}{\sum Rf_{i,l}} \quad (2)$$

The individual ratios $k_{i,l}$ of styrene in the 100 %SBR and NR/SBR blends for all loops are summarized in Table 3.

Profiles of styrene (for NR/2.5 % SBR blend and 100 % SBR) and limonene (for NR/2.5 % SBR blend) using $k_{i,l}$ and the TG curves of NR/2.5 % SBR blend and 100 % SBR as a function of temperature are shown in Fig. 6.

From the emission profile, limonene (NR-specific decomposition product) evolved at its maximum at earlier

temperature than styrene (SBR-specific decomposition product).

Styrene profiles from the 100 % SBR sample and the NR/2.5 % SBR have the same characteristics, i.e., Gaussian with identical temperatures and the same maximum emission profile. These characteristics are essential for the quantification of SBR in the NR/SBR samples.

Quantification of SBR

Styrene which is a specific decomposition product of SBR in the NR/SBR samples is used to quantify the amount of SBR in the blends.

The response factors of styrene, $Rf_{i,l, std}$ for the 100 % SBR are used as a standard.

Using all loops in which styrene is detected, the weighted average amount of SBR, ζ and its weighted standard deviation σ are calculated using $k_{i,l}$ as weighted factor:

$$\zeta = \frac{\sum \left(\frac{Rf_{i,l}}{Rf_{i,l, std}} \cdot k_{i,l} \right)}{\sum k_{i,l}} \quad (3)$$

$$\sigma = \sqrt{\frac{k_{i,l} \cdot \left(\frac{Rf_{i,l}}{Rf_{i,l, std}} - \zeta \right)^2}{\frac{(N-1)}{N} \sum k_{i,l}}} \quad (4)$$

with the N the number of nonzero masses.

Table 4 summarizes the SBR content results of the duplicate experiments in all NR/SBR blend samples. The results show that the SBR content agrees with the formulation within the experimental errors.

Table 3 Ratio k_1 of styrene in the NR/SBR blends for all loops

Loop #	Temperature/°C	100 % SBR	2.5 % SBR	5.5 % SBR	7.5 % SBR
2	260	0	0	0	0
3	280	0	0	0	0
4	300	0	0	0	0
5	320	0	0	0	0
6	330	0.0142	0.0152	0.0154	0.0136
7	340	0.0396	0.0393	0.0429	0.0327
8	350	0.0644	0.0597	0.0614	0.0575
9	360	0.0863	0.0876	0.0919	0.0799
10	370	0.1003	0.1106	0.1097	0.1010
11	380	0.1108	0.1366	0.1210	0.1260
12	400	0.1294	0.1451	0.1454	0.1459
13	420	0.1617	0.1597	0.1591	0.1430
14	440	0.1587	0.1473	0.1464	0.1371
15	460	0.1346	0.0989	0.1068	0.1098
16	500	0	0	0	0

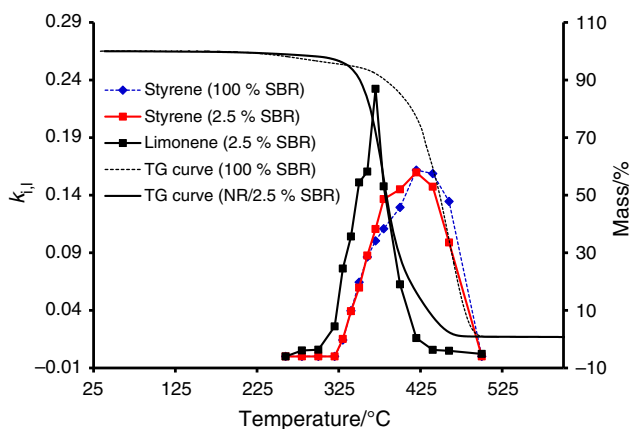


Fig. 6 TG curves of NR/2.5 % SBR blend and 100 % SBR and emission profile of styrene (for NR/2.5 % SBR blend and 100 % SBR) and limonene (for NR/2.5 % SBR blend) versus temperature

Table 4 SBR content results for the respective formulation

Sample	Experiments	SBR content	SBR content average
2.5 % SBR	1	2.28 % ± 0.32 %	2.36 % ± 0.54 %
	2	2.43 % ± 0.44 %	
5.5 % SBR	1	5.45 % ± 0.58 %	5.34 % ± 0.78 %
	2	5.22 % ± 0.52 %	
7.5 % SBR	1	6.31 % ± 0.87 %	6.68 % ± 1.27 %
	2	7.05 % ± 0.92 %	

Conclusions

A novel system to couple a TG to GC/MS by the heated storage interface (IST) offers the possibilities to store fractions of the volatile decomposition products in loops at predefined TG temperature. The stored gases are injected individually to the GC after collection. The gases are first separated by the GC and analyzed by the MS detector. It allows the emission profile of selected evolved compounds as a function of the thermogravimetric decomposition temperature. Here the amounts of very low-content styrene–butadiene (SBR) in natural rubber (NR)/styrene–butadiene (SBR) blends were determined. Investigations by this laboratory by DSC, DMA, TG–MS, TG–FTIR, TG–MS and ATR did not successfully reveal the presence of SBR. Thanks to the chromatographic separation and storage at different temperatures, SBR was detected and its content in individual blend was determined. The results show good agreement with the elastomer formulation. Even the blend containing the lowest amount of SBR content of 2.5 % is clearly quantified.

References

1. Coleman MM, Painter PC. Infrared-absorption spectroscopy, vol. 8. 2nd ed. New York: Wiley; 1986. p. 69–101.
2. Painter PC, Coleman MM, Koenig JL. The Theory of vibrational spectroscopy and its application to polymeric materials. New York: Wiley; 1982.

3. Coleman MM, Painter PC. Fourier transform infrared spectroscopy: probing the structure of multicomponent polymer blends. *Appl Spectrosc Rev.* 1984;20:255–436.
4. George S, Varughese KT, Thomes R. Thermal and crystallisation behaviour of isotactic polypropylene/nitrile rubber blends. *Polymer.* 2000;41:5485–500.
5. Grassie N. *Developments in polymer degradation*, vol. 1–7. London: Applied Science; 1998.
6. Lallandrelli LC, Immirzi Barbara, Malinconico Mario, Martuscelli Ezio, Riva Fernando. Structural and thermal investigations on aromatic polyoxadiazole/polyamide 6 blends. *Macromol Chem.* 1992;193:669–79.
7. Marsh PA, et al. Fundamentals of electron microscopy of heterogeneous elastomer blends. II. *Rubber Chem Technol.* 1968;41:344–55.
8. Freeman WJ. *Characterization of polymers*, vol. 3. 2nd ed. New York: Wiley; 1986. p. 291–327.
9. Irwin WJ. Analytical pyrolysis—an overview. *J Anal Appl Pyrolysis.* 1979;1:3–25.
10. Wolf CJ, Grayson MA, Fanter DL. Pyrolysis gas chromatography of polymers. *Anal Chem.* 1980;52:348A–58A.
11. Irwin WJ. Analytical pyrolysis—an overview. *J Anal Appl Pyrolysis.* 1979;1:89–122.
12. Liebman SA, Levy EJ. Pyrolysis gas chromatography, mass spectrometry, and Fourier transform IR spectroscopy. *Adv Chem Ser.* 1983;203:617–24.
13. Bayer FL. Pyrolysis gas chromatographic characterization, differentiation, and identification of biopolymers—an overview. *Adv Chem Ser.* 1983;203:693–704.
14. Reiner E, Moran TF. Pyrolysis/gas chromatography/mass spectrometry of biological macromolecules. *Adv Chem Ser.* 1983;203:703–17.
15. Giddings JC. The conceptual basis of field-flow fractionation. *J Chem Educ.* 1973;50:667–9.
16. Giddings JC, Meyers MN, Yang FJF, Smith LK. Mass analysis of particles and macromolecules by field-flow fractionation. New York: M. Kerker; 1976. p. 381–98.
17. Tsuge S, Ohtani H. *Basic and databook of pyrolysis chromatography for polymer.* Tokyo: Technosystem; 1995.
18. Pavia DL, Lampman GM, Kriz GS. *Introduction to spectroscopy.* 2nd ed. Philadelphia: Harcourt Brace College Publishers; 1996.
19. Tsuge S, Ohtani H. Structural characterization of polymeric materials by pyrolysis-GC/MS. *Polym Degrad Stab.* 1997;58:109–30.
20. Audebert R. Pyrolytic and gas phase chromatographic study of polymers. *Ann Chim (Paris).* 1968;3:49–66.
21. Cianetti E, Pecci G. Identification of elastomers by gas chromatography of pyrolysis products at a given temperature. *Ind Gomma.* 1969;13:45–54.
22. Ghebremeskel GN, Shield SR. Characterization of binary/tertiary blends of SBR NBR and PVC by IR spectroscopy. *Rubber World.* 2003;227:26–30.
23. Shield SR, Ghebremeskel GN. Use of mid- and near-infrared techniques as tools for characterizing blends of copolymers of styrene-butadiene and acrylonitrile-butadiene. *J Appl Polym Sci.* 2003;88:1653–8.
24. Maurer JJ. Advances in thermogravimetric analyses of elastomer systems. *J. Macromol Sci Chem Part A.* 1974;8:73–82.
25. Brazier DW, Nickel GH. Thermoanalytical methods in vulcanizate analysis II. Derivative thermogravimetric analysis. *Rubber Chem Technol.* 1975;48:661–77.
26. Sircar AK, Lamond TG. Identification of elastomers in tire sections by total thermal analysis. I. Tread and black Sidewall. *Rubber Chem Technol.* 1975;48:301–9.
27. Amraee LA, Kathab AA, Aghafarajollah S. Qualitative and quantitative analysis of SBR/BR Blends by thermogravimetric analysis. *Rubber Chem Technol.* 1996;69:130–6.
28. Shield SR, Ghebremeskel GN. Determination of the styrene content of styrene-butadiene rubber using TGA. *Rubber World.* 2000;223:24–66.
29. Shield SR, Ghebremeskel GN. Pyrolysis-GC/MS and TGA as Tools for characterizing blends of SBR and NBR. *Rubber Chem Technol.* 2001;74:803–14.
30. Ghebremeskel GN, Hendrix C. Analyzing compounds using pyrolysis method. *Rubber Plast News.* 1998;27:28–31.
31. Compton DAC, Johnson DJ, Mittleman ML. Integrated TGA-FTIR system to study polymeric materials—II. *Res Dev.* 1989;31:68–73.
32. Compton DAC, Johnson DJ, Mittleman ML. Integrated TGA-FTIR system to study polymeric materials—I. *Res Dev.* 1989;31:142–7.
33. Dollimore D, Gamlen GA, Taylor TJ. Mass spectrometric evolved gas analysis—An overview. *Thermochim Acta.* 1984;75:59–69.
34. Friedman HL. Mass spectrometric thermal analysis: a review. *Thermochim Acta.* 1970;1:199–221.
35. Perret B, Schartel B. TGA-FTIR: from the investigation of pyrolysis to the elucidation of fire retardancy mechanisms. *Mettler Toledo UserCom.* 2010;32:16–9.
36. Shin T, Hajima O, Chuichi W, Shin T, Hajima O, Chuichi W, editors. *Pyrolysis-GC/MS data book of synthetic polymers.* Amsterdam: Elsevier; 2011.
37. Wang FC-Y. Polymer additive analysis by pyrolysis-gas chromatography I. Plasticizers. *J Chromatogr.* 2000;883:199–210.
38. Wang FC-Y. Polymer additive analysis by pyrolysis-gas chromatography. II. Flame retardants. *J Chromatogr.* 2000;886:225–35.
39. Wang FC-Y. Polymer additive analysis by pyrolysis-gas chromatography IV. Antioxidants. *J Chromatogr.* 2000;891:325–36.
40. Wampler TP. *Applied pyrolysis handbook*, CRC Press. BocaRaton: Taylor & Francis; 2007.
41. Chung HL, Aldridge JC. On-line thermogravimetry/gas chromatography/mass spectrometry. *Instrum Sci Technol.* 1992;20:123–35.
42. Whiting LF, Langvardt PW. On-column sampling device for thermogravimetry/capillary gas chromatography/mass spectrometry. *Anal Chem.* 1984;56:1755–8.
43. McClennen WH, Buchanan RM, Arnold NS, Dworzanski JP, Meuzelaar HLC. Thermogravimetry/gas chromatography/mass spectrometry and thermogravimetry/gas chromatography/Fourier transform infrared spectroscopy: novel hyphenated methods in thermal analysis. *J Anal Chem.* 1993;65:2819–23.
44. Costa L, Camino G, Trossarelli L. Combined thermogravimetry-high-resolution gas chromatography for polymer degradation studies. *J Chromatogr.* 1983;279:125–31.
45. Letoffe JM, Sigala C, Chiriack R, Dutheil C, Carre J. Caractérisation des mélanges complexes d'effluents gazeux par couplage TG/GC-MS. *J Therm Anal Calorim.* 2004;76:491–505.
46. NIST Standard Reference Database 1A, NIST/EPA/NIH Mass Spectral Database (NIST 11) and NIST Mass Spectral Search Program (Version 2.0 g).